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Heat Treatment Impact on the Properties of Na and N Dual Doped ZnO Thin Flms by Spray Pyrolysis

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Abstract

Nano-crystalline *p*-type dual acceptor doped ZnO (ZnO:(Na, N)) thin films are prepared through the spray pyrolysis technique using zinc acetate dehydrate as a starting material. The as-prepared films are annealed at different temperatures, 350 °C, 400 °C and 450 °C for 1h. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive x-ray Spectroscopy (EDX), UV-VIS Spectroscopy and Hall measurement are used to study the structural, surface morphology, optical and electrical properties of the annealed films, respectively. As prepared ZnO:(Na, N) thin films at 350 °C exhibit *p*-type conductivity, while the samples annealed at 400 °C and 450 °C are converted in to n-type conductivity. The lowest resistivity of $5.60 \times 10^{-2} \Omega \text{ cm}$ achieved with a high carrier concentration of $3.15 \times 10^{18} \text{ cm}^{-3}$ for the films annealed at 350 °C.

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Keywords: Spray pyrolysis, Dual doped ZnO, XRD, SEM, Transmittance, p-type conductivity,

1. Introduction

ZnO has triggered worldwide research interest as a wide-band-gap (3.37 eV) semiconductor material (Krajewski et al., 2005) for applications in optoelectronic systems, such as photo detectors (Liang et al., 2001), light emitting diodes (Chen et al., 2000), electro luminescence devices (Miyata et al., 1994), solar cells (Birkmire et al., 2001)

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and flat display devices (Chen et al., 2001). In order to develop the ZnO based optical devices, the first step is the deposition of high quality *n*- and *p*-type ZnO thin films. ZnO has higher exciton binding energy (60 meV) and optical gain (300 cm^{-1}) than those of GaN (Krajewski et al., 2005). The textured ZnO films have been reported to probably have higher quantum efficiency than GaN. Based on these features, ZnO has been a prime candidate for the next generation UV semiconductor laser and light emitting diodes (Yu et al., 1996). To fabricate ZnO *p*-*n* homojunctions required by optoelectronic devices, the realization of *p*-type conductivity is indispensable. However, the difficulty in *p*-type doping of ZnO was still a key bottleneck in optoelectronic applications. Many groups reported that the *p*-type behaviors of ZnO could be unstable and even disappear over time (Barnes et al., 2005; Wang et al., 2003). Dual-doping was a novel method that may fabricate stable *p*-type ZnO. It has attracted attention in recent years (Krtschil et al., 2005; Wang et al., 2006). In most dual doping studies, N and Li (group-IA) were used as the acceptor elements. N was a good group-V acceptor element for ZnO. However, lithium may prefer to be on interstitial site in ZnO lattice and was more easily to form $\text{Li}_{\text{Zn}}\text{-Li}_i$, $\text{Li}_{\text{Zn}}\text{-H}$ complexes (Tomzig et al., 1976; Cox et al., 1978) compared with sodium (Na), since the atomic radius and formation energy of lithium was small compared to sodium. Mono-doped *p*-type ZnO:Na films have been successfully fabricated (Kang et al., 2006; Kim et al., 2009). This indicates that sodium doped ZnO films may be more advantageous in the performance of *p*-type behavior.

Various techniques have been used to deposit undoped and doped ZnO films on different substrates, including sol-gel process (Cai et al., 2009), chemical vapor deposition (Lu et al., 2007), pulsed laser deposition (Jelink et al., 2005), sputtering (Cai et al., 2009), and spray pyrolysis process (Swapna et al., 2013). Among these, the spray pyrolysis technique was credited with several advantages, such as deposition of high purity, cheaper, large-area films at relatively low temperatures. In this work, we have fabricated *p*-type ZnO:(Na,N) thin films by spray pyrolysis. The effects of annealing temperature on the structural, electrical, and optical properties of *p*-type ZnO:(Na,N) films were systematically studied. The performance of optoelectronic devices was predominantly determined by the fundamental properties of materials. Thermal annealing was a widely used method to optimize the complete growth procedure and to achieve the desired properties. Optical and electrical properties of ZnO were sensitive to the annealing treatment, because these properties change significantly with the absorption/desorption of oxygen, the activation of dopants and others processes, which occur during annealing. Several groups have reported the strong influence of annealing conditions, such as the annealing ambient, i.e., in air, N_2 , H_2 , Ar, O_2 or in vacuum and the annealing temperature, on electrical and optical properties of ZnO films (Lin et al., 2001; Shi et al., 2002; Ogata et al., 2000; Wang et al., 2005). However, in most cases, the annealing temperature was much higher than the deposition temperature of the films and the annealing duration was very long. These approaches can cause the solid phase reaction and diffusion between the substrate materials and thin films.

2. Experimental Work

Na-N dual acceptor doped ZnO thin films were prepared via a spray pyrolysis method. The aqueous solution was prepared by dissolving 0.1M zinc acetate di-hydrate (Sigma-Aldrich, 99.5%) in a 90 ml deionized water and 10 ml ethyl alcohol (Merck, 99.9%). The concentration of zinc acetate di-hydrate was 0.1 mol/L. Sodium acetate (Merck, 98.5%) and ammonium acetate (Sigma-Aldrich, 98.5%), as silver and nitrogen sources, were added to the solution. The atomic ratio of Na and N in the solution was adjusted to 6:2. The solution was stirred at room temperature for 30 to 45 min. Before deposition, the glass substrates were cleaned with detergent solution and deionized water. Ultrasonic cleaning was carried out for 30 min and then rinsed in acetone for 10 min. The substrates were glass substrates with dimension 2.5 cm x 1.5 cm x 0.1 cm, and were placed in the surface of a substrate heater when sprayed (Swapna et al., 2014). During spray pyrolysis deposition, a precursor solution was sprayed as fine droplets onto a heated substrate. The atomization of the chemical solution into a spray of fine droplets was effected by the spray nozzle, with the help of compressed air as carrier gas. When the droplets reach the heated substrate, they spread out and undergo pyrolytic decomposition. Finally, the solid compounds react to become a new chemical compound. The spray deposition was carried out at a substrate temperature of 350 °C for 3 min. The spray rate was about 3 ml/min through the nozzle ensures a uniform film thickness. After deposition, all the samples were annealed in air for 1 h at different temperatures (350 °C, 400 °C and 450 °C) for 60 min. The thickness of the films was approximately 987 nm as measured by stylus profile meter. The electrical

properties of the films were investigated by Hall-effect measurement system (Ecopia: HMS 5000) using the Van der Pauw configuration. The structural characterization was carried out by X-ray diffraction (XRD) measurements. The X-ray diffraction (XRD) patterns of the films were recorded with a Rigaku X-ray diffractometer (D/Max ULTIMA III, Rigaku, Japan) operating with a 1.5406 \AA monochromatized $\text{CuK}\alpha$ radiation at 40 kV and 30 mA. The surface morphology of the samples was investigated by Hitachi-S3000N scanning electron microscopy (SEM). The electrical resistivity of the prepared films was measured by the Van der Pauw four-probe method. Transmission, T, and reflection, R, spectra of the prepared samples were measured by incidence of light, using a double beam Shimadzu UV-Vis-1700 spectrophotometer, in the wavelength range 300-1000 nm.

3. Results and discussion

3.1 Electrical characteristics

The electrical properties are measured by Hall-effect measurement system for the $\text{ZnO}:(\text{Na},\text{N})$ films prepared at different annealing temperatures and thus obtained results are illustrated in Table 1. The measurement results show that the as-deposited $\text{ZnO}:(\text{Na},\text{N})$ film is *p*-type. The as-prepared films show *p*-type conductivity with increase of hole concentration upon dual acceptor doping (Swapna et al., 2013a), which is due to the formation of acceptor-acceptor ($\text{Na}_{\text{Zn}}\text{-N}_{\text{O}}$) complex. Both Na_{Zn} and N_{O} are acceptor impurities in ZnO and the $\text{Na}_{\text{Zn}}\text{-N}_{\text{O}}$ complex is believed to be the acceptor in $\text{ZnO}:(\text{Na},\text{N})$ responding to the *p*-type conductivity. In this regard, the degradation of *p*-type behaviors at high temperatures could be explained by the dissociation of $\text{Na}_{\text{Zn}}\text{-N}_{\text{O}}$ complexes producing various compensating donors in ZnO (Lee et al., 2001; Wardle et al., 2005).

It is observed that after the air annealing, the conduction type of the $\text{ZnO}:(\text{Na}, \text{N})$ films changed from *p*-type to *n*-type. It could also be seen that the resistance of the films firstly increases with the increase of annealing temperature, then become significantly decrease when the annealing temperature reach to 450°C . The lowest resistivity of $5.60 \times 10^{-2} \Omega\text{cm}$ achieved with a carrier concentration of $3.15 \times 10^{18} \text{ cm}^{-3}$ for the as-prepared *p*-type $\text{ZnO}:(\text{Na},\text{N})$ films deposited at a substrate temperature of 350°C . From Table 3, the lowest sheet resistance of as-prepared *p*-type $\text{ZnO}:(\text{Na}, \text{N})$ films is $0.56 \text{ k}\Omega/\square$. After being annealed at 400°C , the $\text{ZnO}:(\text{Na}, \text{N})$ film turned into *n*-type and the sheet resistance is $7.13 \text{ k}\Omega/\square$. As known, the intrinsic conductivity of ZnO is greatly influenced by the point defects produced therein. The *p*-type conductivity of undoped ZnO has been reported to be possibly due to the formation of Zn vacancies (Ma et al., 2004). The previous investigation also demonstrated that intrinsic *p*-type ZnO films with the high hole concentration can be achieved on glass substrate (Huang et al., 2010). The change of electrical property of the films may be explained as followed. When the films are annealed at a temperature of 400°C , some nitrogen escape from the thin film, mainly escape from interstitial site, so the sheet resistance of the film become higher, but the films show *n*-type. However with the further increase of annealing temperature, the crystal quality gradually increases, but more and more nitrogen escape from the film (first from interstitial site, then from replaced site), which result in the change of conduction type from *p*-type to *n*-type. The hole carriers become less and less, which result in the change of conduction type from *p*-type to *n*-type. With regard to the conversion of the conducting type of the films at a higher annealing temperature, it could result from the escape of N acceptors out of the films (Zhang et al., 2006).

Table 1: Carrier concentration (n), Mobility (μ) and Resistivity (ρ) of the $\text{ZnO}:(\text{Na}, \text{N})$ thin films with various annealing temperature

Temperature	Carrier concentration (cm^{-3})	Mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	Resistivity ($\Omega \text{ cm}$)	Carrier type
As-prepared at 350°C	3.15×10^{18}	35.7	5.60×10^{-2}	<i>p</i>
Annealed at 400°C	9.82×10^{18}	9.04×10^{-1}	7.04×10^{-1}	<i>n</i>
Annealed at 450°C	2.88×10^{19}	3.54×10^{-1}	6.12×10^{-1}	<i>n</i>

3.2 Structural analysis

The XRD spectra of Na and N dual acceptor doped ZnO thin films deposited at various annealing temperatures are shown in Fig. 1. A matching of the observed and the standard (hkl) planes confirms that the deposited films are of ZnO having wurtzite structure (Swapna et al., 2013a), and exhibit the polycrystalline in nature. The crystallinity is seen to be increasing as the annealing temperature increases (peak intensities) up to 450°C, indicating the formation of more crystallites with well-defined orientation along (002) plane. Some other prominent peak corresponding to (101) is also present in the XRD spectra (Fig. 1). Dual acceptor doped ZnO films show less intensity peak at (101), and (002) peak intensity is found to be increased in sample prepared at 450°C indicating to the better crystallinity. So it is the optimum temperature to obtain uniform well adherent ZnO film is at 450°C. The crystallite size, D is determined using the Debye–Scherrer formula (Benramache and Benhaoua, 2012):

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Where θ is the Bragg's diffraction angle, $\lambda = 1.5406 \text{ \AA}$ denotes the wavelength of CuK_α radiation, β represents the full-width at half-maximum (FWHM) and k is the Scherrer constant (0.9). The average crystallite size of ZnO:(Na, N) films is 38 nm, 43 nm, and 50 nm, respectively. The crystallite size increases with the increase of annealing temperature. During annealing process the ZnO:(Na, N) films are re-crystallized. Both calculated values of crystallite size and stress effect as function of annealing temperature is shown in Table 2. It is clear that the crystallite size increases with decrease in stress; this is in good agreement with the variation reported elsewhere (Chandramohan et al., 2011).

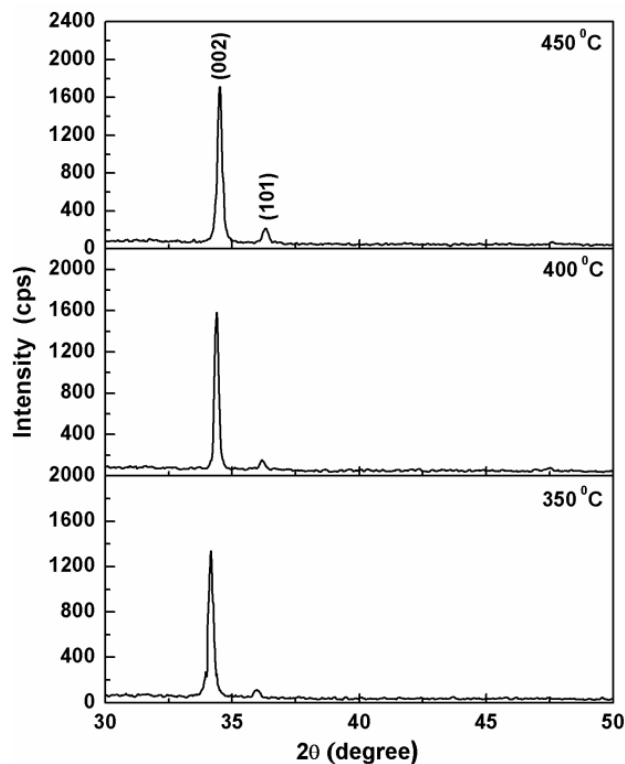


Fig. 1 XRD spectra of ZnO:(Na, N) thin films at different annealing temperatures of 350 °C, 400 °C and 450 °C.

Table 2 shows the d-spacing with respect to dopant concentration, which are calculated using the Bragg's relation ($d = \lambda / 2 \sin \theta$), where λ is the wavelength of the X-ray used and θ is the position of the peak. It is observed that the d-spacing value is high for ZnO:(Na, N) films compared to bulk ZnO of 2.597 Å, (JCPDS card 75-0576). Because, the replacement of Na ions on Zn site and N ions on O site. The ionic radii of Na and N are larger than Zn and O, respectively. Hence, the replacement of larger ion on smaller ionic site increases the d spacing. Therefore it is expected that more Na and N ions have been incorporated at lower concentration. The interval distance 'd' between (002) planes of as-deposited Na-N dual acceptor doped ZnO film is 2.622 Å calculated from XRD data, which is larger than the bulk value of 2.597 Å, (JCPDS card No. 75-0576). When the sample annealed at 450 °C, the d value decreased to 2.599 nm, close to the value of bulk ZnO. This indicated that the films deposited by spray pyrolysis method are under a compressive stress in the film plane.

Table 2: Calculated Crystallite size, TC, d-spacing and stress values of ZnO:(Na, N) thin films with different annealing temperature.

Temperature	Crystallite size (nm)	Texture coefficient TC	d-spacing (Å)	stress (Gpa)
As-prepared at 350 °C	43	2.51	2.622	-4.474
Annealed at 400 °C	49	2.74	2.606	-1.592
Annealed at 450 °C	56	2.98	2.599	$-(1.86 \times 10^{-2})$

In order to quantitatively, evaluate the orientation of films crystallites, the texture coefficient, TC(hkl), has been calculated from the XRD spectra (Ramadan et al., 2009). We take into account two important diffraction peaks (002) and (101), respectively and the values of TC(hkl) have been determined from the expression (Eq. (2)).

$$TC(hkl) = \left(\frac{\frac{I_{(hkl)}}{I_{o(hkl)}}}{\frac{1}{N} \sum \frac{I_{(hkl)}}{I_{o(hkl)}}} \right) \quad (2)$$

where TC is the texture coefficients of the (hkl) plane, I is the measured intensity, I_0 is the ASTM standard intensity and N is the reflection number. From this definition it is clear that the deviation of the texture coefficient from unity implies the preferred orientation of the growth. The higher deviation of the texture coefficient from unity indicates the higher preferred orientation of the film. Analyzing the values of TC(hkl), from Table 2, it can be concluded that both the nature of the substrate and the annealing temperature may influence the preferential orientation of the crystallites. Some parameters such as interaction between the deposited material and the substrate type, the annealing temperature or other deposition conditions can influence the film crystallization and crystallites having other orientation may grow (Rusu et al., 2007; Kazmerski, 1980; Jagadish, 2009). From Table 2, the texture coefficient for all the film has relatively higher value along the (002) plane than the other plane (101). The texture coefficient of (101) has a minimum value in all the sprayed ZnO:(Na,N) films.

3.3 Optical studies

The optical properties of Na-N dual acceptor doped ZnO thin films are investigated using the transmission and reflection of the spectra (Fig. 2) observed in the wavelength range 300-1000 nm. ZnO:(Na,N) thin films prepared at various annealing temperatures for a deposition time of 3 min. In general, in the visible region of the spectra, the transmission is very high (high enough to observe interference fringes). It is due to the fact that the reflectivity is low and there is no (or less) absorption due to transfer of electrons from the valence band to the conduction band

owing to optical interference effects, it is possible to maximize the transmission of thin film at particular region of wavelengths. It can be observed that an increase in annealing temperature improves the transmission. The sharp ultraviolet absorption edge is observed at approximately 378 nm in the UV region. The average optical transmittance and the estimated E_g values are 90% and 3.71 eV, respectively. The figure of merit (FOM) has been a common rating method for TCO films for their possible use in solar cell applications. The device performance is determined from FOM (Haacke, 1976):

$$\phi_{TC} = \frac{T^{10}}{R_{sh}} \quad (3)$$

Sheet resistance (R_{sh}) is a useful parameter in comparing thin films, particularly, those of the same material deposited under similar conditions. R_{sh} is found to be minimum ($5.67 \times 10^2 \Omega/\square$) for the film deposited at 350 °C. Both low resistivity and high transmittance are equally important for TCO layers, especially in the case of solar cell applications. TCO material must necessarily represent a compromise between electrical conductivity and optical transmittance. The Haacke's figure of merit (Haacke, 1976) is a good criterion to define the quality of highly transparent and conductive thin films. The doubly doped ZnO:(Na,N) film prepared in this study is found to has desirable FOM value (Table 3) suitable for optoelectronic device applications.

Table 3: Calculated Sheet resistance, FOM values of ZnO:(Na, N) thin films with various annealing temperature.

Temperature	Sheet Resistance ($\times 10^2 \Omega/\square$)	FOM ($\times 10^{-3} \Omega^{-1}$)
As-prepared at 350 °C	5.67	1.18
Annealed at 400 °C	71.32	6.43×10^{-2}
Annealed at 450 °C	62.00	7.86×10^{-2}

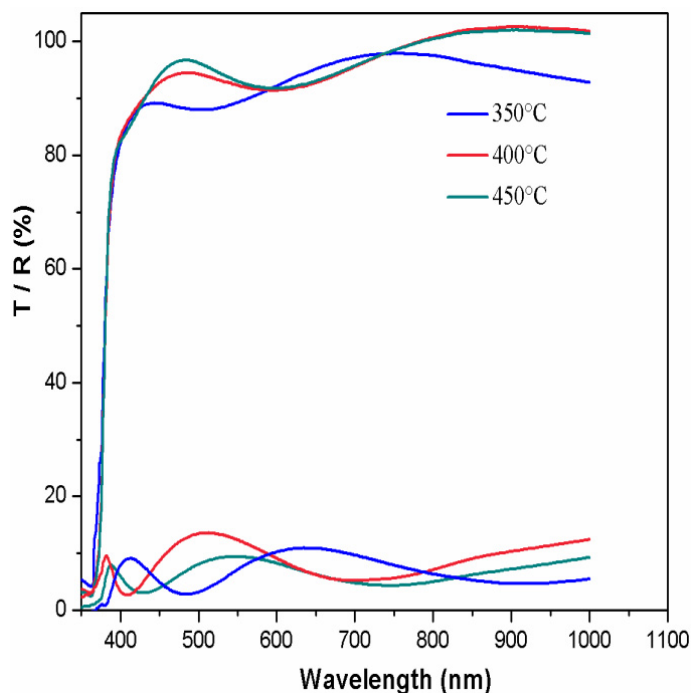


Fig. 2 Optical transmittance and reflectance spectra of as-prepared (350 °C) and annealed (400 °C and 450 °C) ZnO:(Na, N) thin films.

3.4 Surface morphology and Compositional analysis

Fig. 3 shows the comparative morphology of ZnO:(Na,N) thin film deposited at different annealing temperature between 300 and 500 °C. SEM (Scanning electron microscopy) morphological studies show a dense nano rod-like structure with length in the range of 171.8 nm and diameter of the order of 54.1 nm. Dual acceptor doped ZnO films deposited at 350 °C, 400 °C, 450 °C (Fig. 3a, 3b and 3c) show nearly similar morphology, smooth deposition without the formation of distinct grains. At higher deposition temperature of 450 °C (Fig. 2c), doped zinc oxide films show an increase in grain size. These results are in supported with structural studies. The EDX analysis give the presence of Zn, O, Na and N for the as-prepared ZnO:(Na, N) films is shown in Fig. 3d. The chemical compositions of the Zn, O, Na and N in the sample are identified as 16.76, 57.56, 24.38 and 1.31 at.%, respectively.

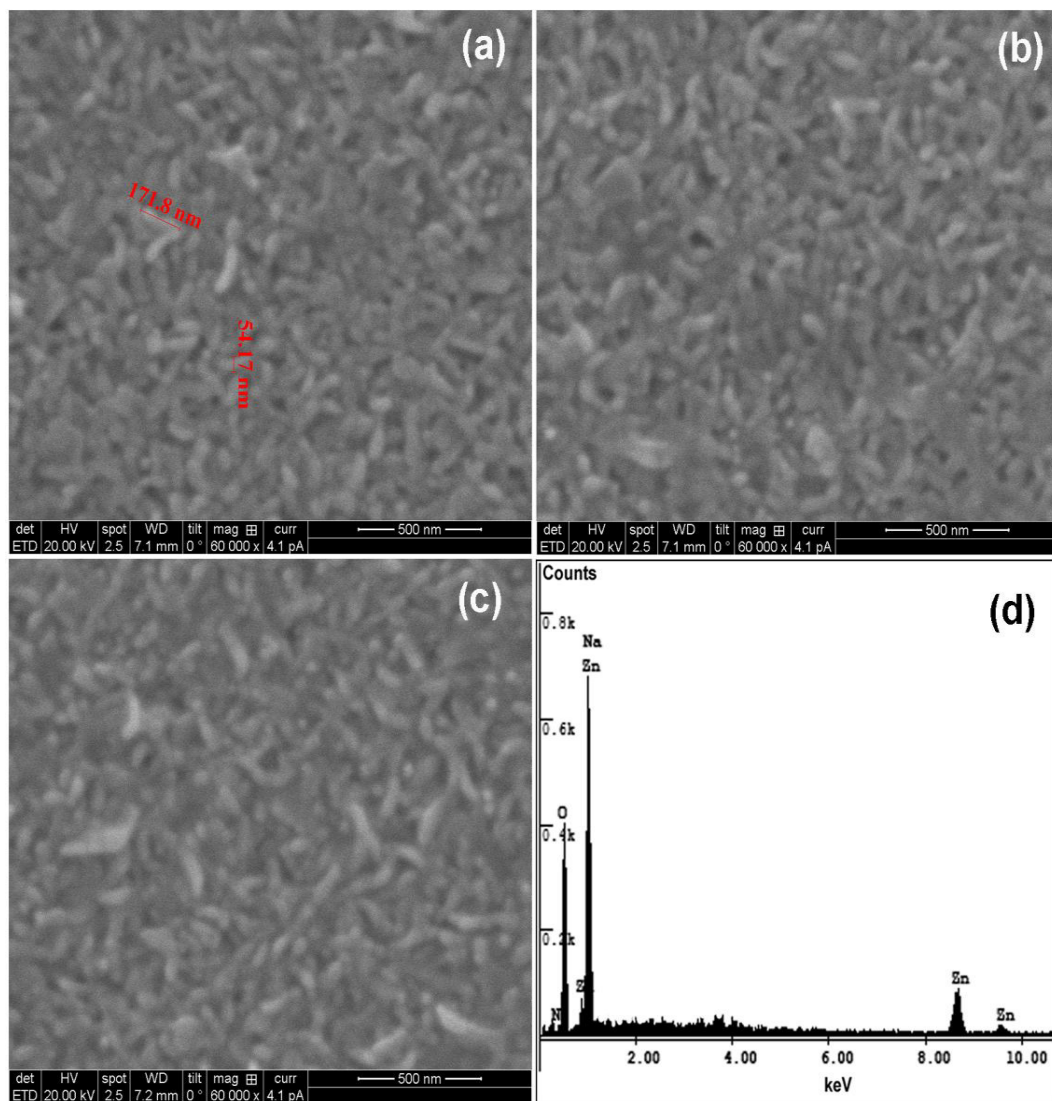


Fig. 3 SEM micrographs of ZnO:(Na, N) films at different annealing temperatures of (a) 350 °C, (b) 400 °C, (c) 450 °C and (d) EDX spectrum of ZnO:(Na, N) films at 350 °C.

4. Conclusions

In this study, p-type ZnO films with excellent electrical properties were prepared by spray pyrolysis combined with a Na–N dual doping technique. A dual acceptor doping approach has been proposed to realize p-type ZnO. The influence of post-growth annealing conditions, i.e., annealing temperature, on structural, optical and electrical properties of p-type ZnO films is investigated. XRD measurements show that all the films are nanocrystallized in the hexagonal wurtzite structure and present a preferred orientation. The maximum crystallite size of the (002) plane is found to be 56 nm. The high resolution SEM studies show the similar in film surface morphology and observed the nano-rod like structures. The lowest sheet resistance of as-prepared p-type ZnO:(Na, N) film is 0.56 k Ω/\square . After being annealed at 400 °C, the ZnO:(Na, N) film turned into n-type and the sheet resistance is 7.13 k Ω/\square . The average transmittance is about 90% for ZnO:(Na, N) samples in the visible region.

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